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Boron-Content Profile of a Boron-Pyrolytic Graphite Nose Cone Model

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Prepared for BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS
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LOS ANGELES AIR FORCE STATION
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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. AF 04(695)-669.

This report, which documents research carried out from 2 January 1966 through 15 May 1966, was submitted on 3 August 1966 to Captain Robert F. Jones, SSTRT, for review and approval.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Robert F. Jones, Capt., USAF
Space Systems Division
Air Force Systems Command

ABSTRACT

The pyrohydrolysis method of determining boron concentration in boron-pyrolytic graphite was evaluated by the analysis of reference samples. The method was found to be applicable and was applied to the determination of the boron-content profile of a boron-pyrolytic graphite nose cone model fabricated by the graded boron composition technique. The results of the analysis conclusively show that the expected boron concentration gradient is absent and that effects on fabricability have been incorrectly attributed to such a secondary anisotropy. Kinetic arguments which favor the existence of the concentration gradient also remain open to question.

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I. INTRODUCTION

Considerable effort has been expended in the detailed evaluation of the physical, mechanical, and chemical properties of boron-pyrolytic graphite nose cones.[1] However, precise correlations between the measured properties and the boron concentrations have not been established simply because an analytical technique of high accuracy and precision was not available. Recently much faith has been placed on the graded boron composition technique of fabricating nose cones. In this technique, the ability to fabricate crack-free and delamination-free nose cones is attributed to secondary anisotropy (Ref. 1) introduced into the cone by establishing a boron concentration gradient of 1.5 to 0.1 percent from the outer to the inner shell. Nonetheless, the existence of this gradient has not been experimentally verified.

It is the purpose of this report to demonstrate the applicability of the recently developed pyrohydrolysis method (Ref. 2) for the determination of boron concentration in boron-pyrolytic graphite and to show conclusively that the expected boron concentration gradient is not present in the boron-pyrolytic graphite nose cone model that had been fabricated by the graded boron composition technique.

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[1] ASTM Pyrolytic Graphite Symposium, 10-11 May, 1966, Palm Springs, California.

II. EXPERIMENTAL

A. APPARATUS AND MATERIALS

The apparatus and the general analytical procedures of the pyrohydrolysis method used in this investigation have been described in Ref. 2. Only one minor modification was made in the present procedure. Sodium hydroxide solutions were prepared from Acculate[2] standard solutions and re-standardized with potassium hydrogen phthalate.

Reference boron-pyrolytic graphite plates of nominal boron contents of 0, 0.3, 1, 2, and 4 percent by weight were purchased from Raytheon Company. These plates were specially fabricated at a deposition temperature of 1850°C and a system pressure of 5 to 20 torr. The source of carbon was methane, and the source of boron was trimethyl borate.

Ten pieces of nose cone models and a whole nose cone model (PG 5024) were obtained from General Electric Company through the AFML Program Office. The ten samples were taken from the outer 50 mils of the nose cone models. Nose cone model PG 5024 was prepared by the graded boron composition technique by deposition on a female mandrel. The BCl_3 pressure of the feed stream was varied in stepwise fashion during the deposition process so that the boron content of the nose cone model would vary from 1.5 to 0.1 percent from the outer to the inner shell.[3]

B. SAMPLE PREPARATION

Sections (1/8 in. thick, 1/4 in. long and 1 in. wide) were cut from each

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[2]Registered Trade Mark, Anachemia Chemicals, Ltd.

[3]Private communication from Mr. Jerome Persh, General Electric Company, 21 April 1966.

end and the middle of each reference plate and designated as upstream, middle, and downstream. Each of these sections were then ground into powder with a Wig-L-Bug.

The ten nose cone model specimens were ground into powder with a Wig-L-Bug and divided into two portions for duplicate analysis. In the case of the model nose cone PG 5024, samples were taken in such a manner that the boron concentration profile of the cone could be studied. The cone was divided into sections of 1/4 in. or 1/2 in. high frustums as shown in Fig.1 . Except for the tip, where the entire section was utilized as a single sample, samples were taken from each section by milling off a 50-mil depth of the frustum at a time. For a given section, the 50-mil cuts were numerically labeled in consecutive order, i.e., A-1, A-2, A-3, etc., as the cuts were made from the outer to the inner surface of the frustum. In essence, each sample may be regarded as a 50-mil thick frustum of either 1/4 in. or 1/2 in. height.

BORON - PYROLYTIC GRAPHITE NOSE CONE MODEL PG 5024

SECTION	WIDTH, in.
TIP	0.20
A-F	0.25
G-M	0.50
N	0.80

TASK 3-5.1

RUN NO. 9

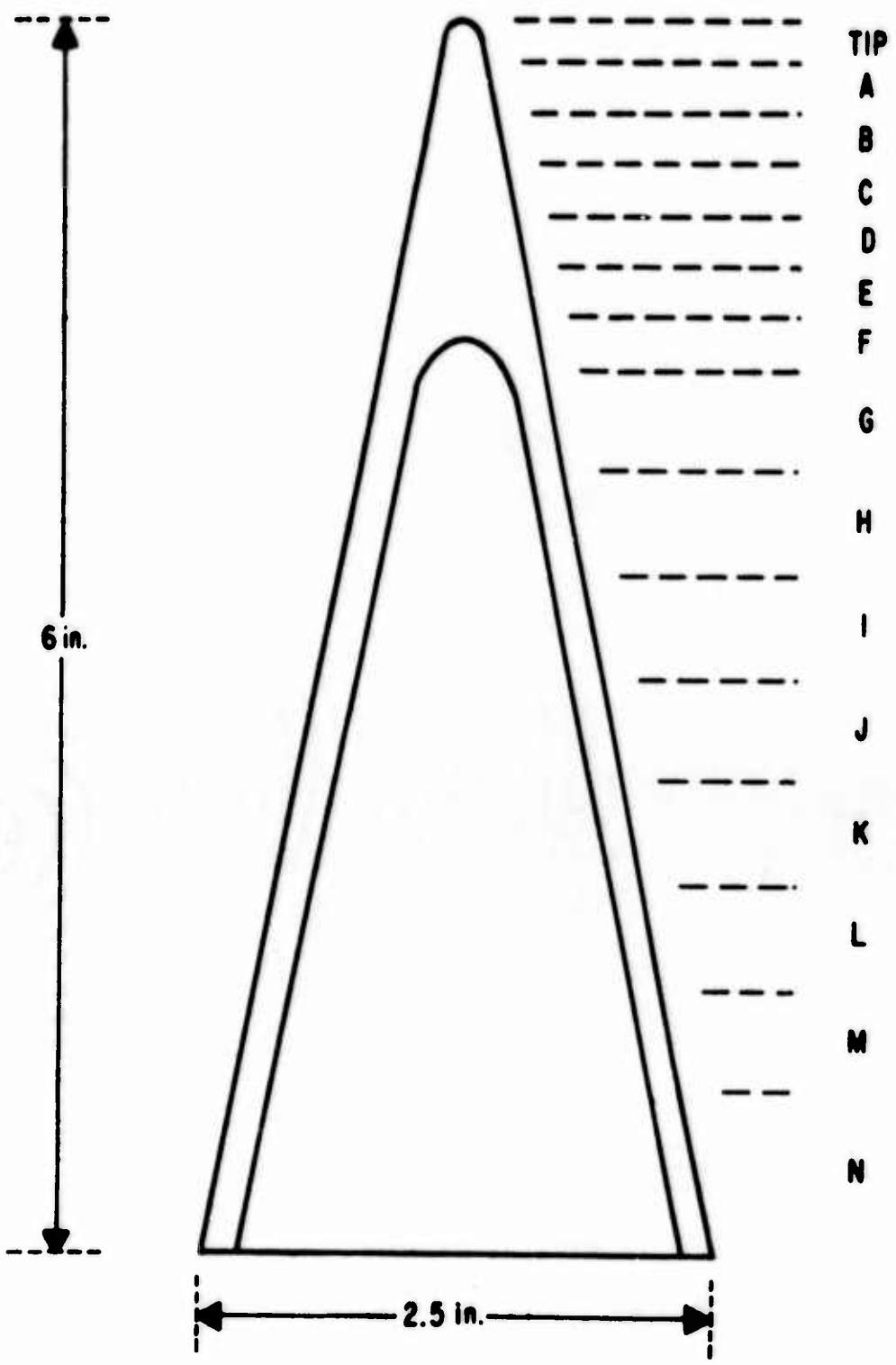

Fig. 1 Identification of Sections of Boron-Pyrolytic Graphite Nose Cone Model

III. RESULTS AND DISCUSSION

In an earlier report (Ref. 2) it was shown that the pyrohydrolysis method of determining boron concentration was capable of high accuracy and precision. These attributes were demonstrated with data obtained on standard samples prepared from boron carbide and ultra pure graphite. However, relatively few data were presented to substantiate the method's applicability to boron-pyrolytic graphite samples. In these samples, the chemical nature of boron (as yet unknown) may be quite different from that of boron carbide and may invalidate the accuracy of this analytical method. In order to ensure that this method is applicable to boron-pyrolytic graphite specimens, regardless of the chemical state of boron, reference samples were analyzed. The results are presented in Table 1 together with the spectrographic data furnished by the manufacturer.

Table 1. Boron Analysis on Reference Samples

Reference Sample (Nominal % B)	Boron, wt %					
	Spectrographic[a]			Pyrohydrolysis		
	Upstream	Middle	Downstream	Upstream	Middle	Downstream
0.3	0.40	--[b]	0.33	0.49	0.40	0.35
1	1.16	1.28	1.04	0.89	0.84	0.80
2	2.48	--	1.28	2.71	2.44	2.32
4	--	--	4.30	5.85	4.53	4.10

[a] Results furnished by Raytheon Company
[b] Not analyzed

The results obtained by the two techniques are in good agreement for the 0.3- and 1-percent reference samples, confirming the applicability of the pyrohydrolysis method to the determination of boron concentration in boron-pyrolytic graphite specimens. The discrepancies in the results for reference samples containing more than 1 percent boron are not too surprising since the accuracy of the spectrographic technique decreases as the boron concentration increases above 1 percent (Ref. 3). In this particular case, the variations may be attributed to errors introduced during the dilution procedure employed to bring the boron concentration within the range compatible with the spectrographic method of analysis. Such errors in the spectrographic analysis are widely recognized[4] and do not detract from the reliability of the present method.

The existence of a concentration gradient in the longitudinal direction of the slab is as expected. The gradient may be attributed to differences in the rate of codeposition of boron due to temperature gradients in the furnace and to the continuing depletion of the boron content of the feed stream. That is, for a given volume element, the boron content of the feed stream continuously decreases due to deposition as it traverses the furnace.

The high precision of this method is illustrated by the data shown in Table 2. High precision is easily attained if the titration variables discussed by Colman and Rigdon (Ref. 4) are carefully controlled.

The analytical data for nose cone model PG 5024, whose boron concentration is presumed to vary from 1.5 to 0.1 percent by weight from the outer to the inner shell of the cone with no variability in the axial direction are given

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[4] Discussions with C. Pappis of Raytheon Company, 26 May 1966.

Table 2. Duplicate Boron Analysis on Boron-Pyrolytic Graphite Nose Cone Models

Sample No.	Boron, wt %	
	Run No. 1	Run No. 2
PG 5019	0.161	0.163
PG 5021	0.140	0.150
PG 5024	0.0747	0.0725
PG 7027	0.579	0.587
PG 7028	0.583	0.583
PG 7029	0.544	0.547
PG 7030	0.502	0.501
PG 7031	0.538	0.540
PG 4022 B	0.390	0.392
PG 4023	0.258	0.254

in Table 3. The same results are presented as boron-content profile in Fig. 2. The following conclusions are evident:

1. The expected boron concentration gradient is absent.
2. The maximum boron concentration is less than 0.5 percent.
3. The boron content varies in the axial direction from approximately 0.3 percent at the apex to 0.06 percent at the base.

No plausible explanation can be given for the absence of the concentration gradient since the kinetics and mechanism of the deposition of boron-pyrolytic graphite are not fully understood. The variability in boron concentration in the axial direction may be ascribed to the continuing decrease in the boron content of the feed stream.

Table 3. Boron Analysis of Nose Cone Model PG 5024

Sample	Boron, wt %	Sample	Boron, wt %
Tip	0.327	E-5	0.168
		E-6	0.139
A-1	0.247	(E-7	0.160
A-2	0.354	E-8)	
A-3	0.408		
(A-4[a]	0.428	F-1	0.112
A-5)		F-4	0.117
		F-6	0.116
(B-4	0.398	(F-7	0.212
B-5)		F-8)	
C-1	0.198	G-1	0.083
C-2	0.308	G-4	0.084
C-3	0.368	G-6	0.168
C-4	0.376		
C-5	0.384	H-4	0.089
C-6	0.340		
		J-1	0.061
D-4	0.320	J-3	0.062
(D-6	0.204		
D-7)		K-1	0.050
		K-3	0.049
E-1	0.142		
E-2	0.208	M-1	0.064
E-3	0.242	M-3	0.054
E-4	0.213		

[a] Brackets indicate that the two portions were combined and analyzed as a single sample.

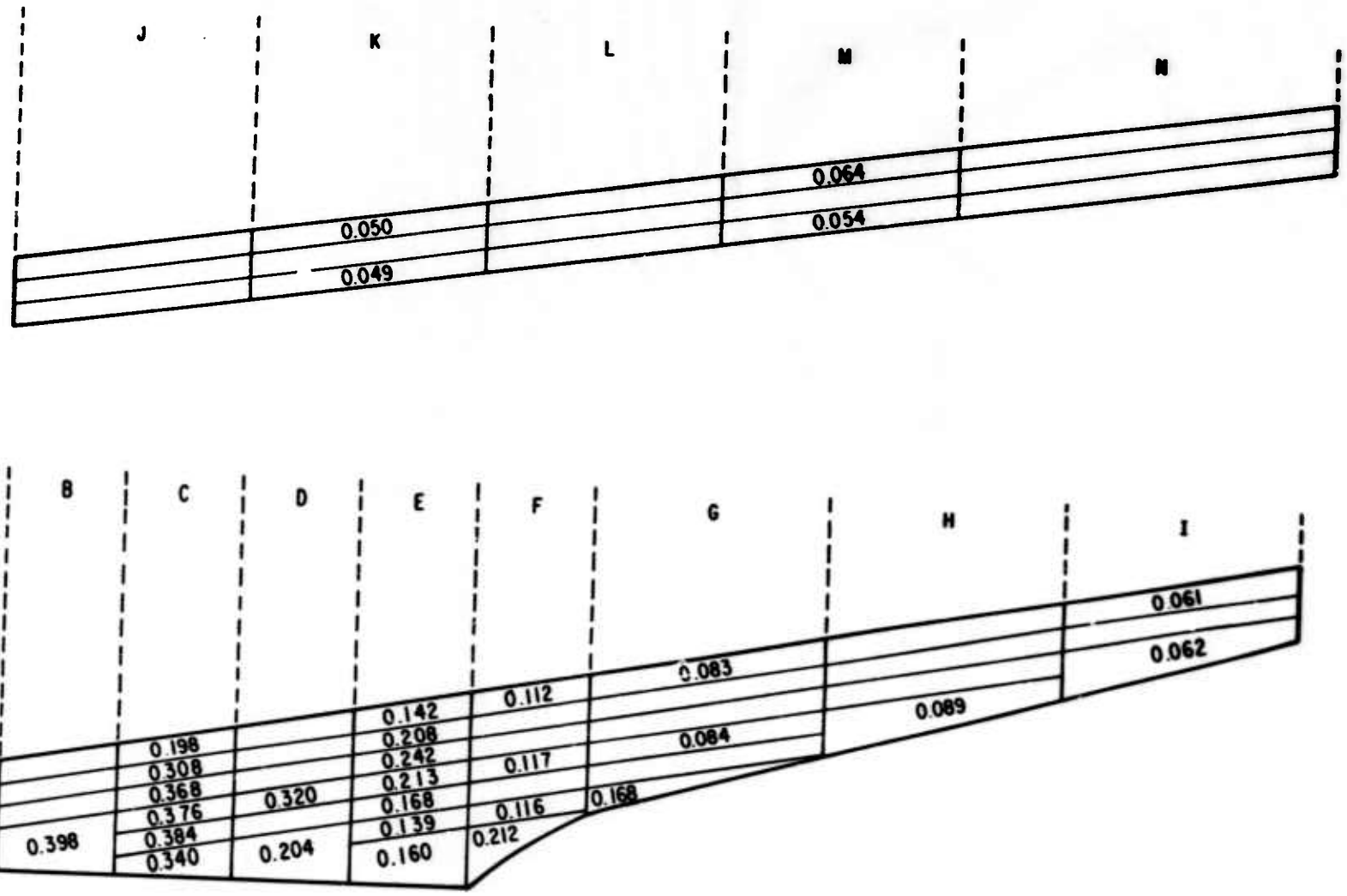

Fig. 2 Boron-Content Profile of Nose Cone Model PG 5024

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